REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-02-

0011

1. REPORT DATE (DD-MM-YYYY) 14/12/2001	**2. REPORT TYPE** Final Technical	1/6/1996 to 31/5/2001
4. TITLE AND SUBTITLE Materials and Processing at the Nanometer Scale		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER F49620-96-1-0035
		5c. PROGRAM ELEMENT NUMBER 61103D
6. AUTHOR(S) Larry R. Dalton		**5d. PROJECT NUMBER** 3484
		5e. TASK NUMBER RS
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Southern California, University Park, Los Angeles, CA 90089		**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 N. Randolph St., Ste 732 Arlington, VA 22203-1977		**10. SPONSOR/MONITOR'S ACRONYM(S)**
12. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited		
13. SUPPLEMENTARY NOTES		

20020130 246

14. ABSTRACT

Researchers supported by the DoD MURI on Materials & Processing at the Nanometer Scale (administered by AFOSR) have pioneered the use of nanoscale "dendrimers" or "tree-like branched molecular structures with each limb designed for a special function" to achieve electronic isolation and directed energy/charge transport. These novel dendrimer materials have been used to develop improved electro-optic modulator materials, light harvesting and optical amplifier materials, high-density electronic memory materials, light emitting diode materials, and two-photon lasing materials. Incorporation of electro-optic organic chromophores into the core of dendrimer materials eliminates quenching of macroscopic electro-optic activity by intermolecular (chromophore) electrostatic interactions.

Other advances involving nanoscale materials include the first demonstration (with Allied Signal Corporation and later Honeywell) of single wall carbon nanotube actuators. Polymer nanospheres have been used to demonstrate high-density erasable optical memories and nanoscale chemical reactors crucial for improving the efficiency of fuel cells. Polymer microsphres have also been used as templates for chemical synthesis and such chemical machining has been used to achieve visible wavelength photonic bandgap materials. Advances have been made in the fabricating of phase-separating block copolymers. Inorganic/organic nanocomposites have been used to fabricate high-density optical memories (including holographic and two-photon memories), organic lasers, and sensor protection materials.

15. SUBJECT TERMS

Nanoscale materials, dendrimers, polymer nanospheres, phase separation block copolymers, nanocomposites, photonic bandgap materials, single wall carbon nanotubes

16. SECURITY CLASSIFICATION OF: Unclassified, Distribution Unlimited			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Larry R. Dalton
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	Distribution Unlimited	50	**19b. TELEPHONE NUMBER** *(include area code)* (206) 543-1686

MATERIALS & PROCESSING AT THE NANOMETER SCALE
F49620-96-1-0035

Final Report

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November 19, 2001

MATERIALS & PROCESSING AT THE NANOMETER SCALE
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Researchers supported by the DoD MURI on Materials & Processing at the Nanometer Scale (administered by AFOSR) have pioneered the use of nanoscale "dendrimers" or "tree-like branched molecular structures with each limb designed for a special function" to achieve electronic isolation and directed energy/charge transport. These novel dendrimer materials have been used to develop improved electro-optic modulator materials, light harvesting and optical amplifier materials, high-density electronic memory materials, light emitting diode materials, and two-photon lasing materials. Incorporation of electro-optic organic chromophores into the core of dendrimer materials eliminates quenching of macroscopic electro-optic activity by intermolecular (chromophore) electrostatic interactions. Dendrimer structures typically permit factor of two improvements in electro-optic activity as well as considerable improvements in chemical stability, optical loss, and material processability. Using this approach, electro-optic modulators characterized by drive voltage requirements of less than 1 volt have been realized. Operation at such low drive voltages is necessary for compatibility with the fastest electronic components. Dendrimer-based electro-optic modulators exhibit operational bandwidths of several hundred gigahertz (more than 100 trillions cycles or bits of information processed per second). Such modulators are likely to be critical components of next generation Internet communication, electronic counter measure, mobile data management platforms, and radar systems. Indeed, Boeing and Motorola are proposing to develop data management components for next generation AWACS using the materials and concepts developed in this program. Other applications include cable television (high speed transmission of video data), high speed switching nodes in fiber optic communication networks, backplane interconnects for high speed computers, ultrafast data processing (e.g., analog to digital conversion), remote voltage sensing, radiofrequency distribution, optical gyroscopes, and improved land mine detection antennae systems.

Electronic isolation achievable with dendrimer structures has also been used to eliminate self- and ligand-quenching of rare earth ion luminescence (light emission), which currently limits the efficiency of fiber optical amplifiers (key elements in the long distance transmission of information). The oscillator strength (intensity of light emission or effectiveness of light amplification) of rare earth ions has been increased by the use of "asymmetric" dendrimers. Light harvesting dendrimers, mimicking the photosynthetic reaction center of green plants, have been prepared that exhibit very efficient harvesting of light over the ultraviolet, visible, and near infrared spectral regions. Such dendrimers have potential applications ranging from photovoltaic cells to fiber optical amplifiers that do not require laser pumping. Light harvesting solar cell coatings, based on new dendrimer materials, have been transitioned to AFRL-Kirtland AFB for evaluation with silicon and GaAS solar cells.

Dendrimers containing variable redox state metal ion cores have been prepared and permit the fabrication of ultrahigh density electronic memories. Although the critical issue of addressing these nanometer scale (trillionth of a meter) memory elements remains to be solved, the fundamental limit on memory size (defined by electron exchange between adjacent memory elements) has been precisely defined. Significant advances have also been realized in AFM nanolithography.

Dendrimer structures have been used not only to spatially direct energy transfer (as in light harvesting dendrimers) but also to direct charge transport. One consequence has been the

development of improved organic light emitting diodes. While organic light emitting diode technology is still in the development stage, this technology may ultimately impact the billion-dollar displays industry.

Record two photon absorption coefficients have been obtained using multi-chromophore dendrimer materials. Finally, control of electronic interactions in dendrimer materials has permitted observation of phenomena such as two-photon lasing, which is not observable in bulk materials. The scientific basis of this exciting observation is now well understood and relates to increasing the lifetime of excited states.

In addition, to pioneering the development of dendrimers for electronic and optical applications, researchers supported by the DoD MURI on Materials & Processing at the Nanometer Scale have realized a number of other noteworthy accomplishments. These include the first demonstration (with Allied Signal Corporation and later Honeywell) of single wall carbon nanotube actuators. These actuators, which are very thermally and mechanically robust, may have applications as nano and mesoscale machines capable of function in the most extreme environments. Optical switching has been demonstrated using these actuators. Polymer nanospheres have been used to demonstrate high-density erasable optical memories (US Patent 5759447 A 980602) and nanoscale chemical reactors crucial for improving the efficiency of fuel cells. Indeed, considerable progress has been made in this MURI on improving the efficiency of a variety of fuel cells. One of the MURI participants, 1994 Nobel Laureate in Chemistry Professor George Olah speaks on the importance of fuel cell technology in the May 24, 1999 issue (page 33) of Chemical & Engineering News. Olah has proposed that a methanol fuel cell under development could be used to improve the efficiency of power plants and to reduce carbon dioxide emissions as well as exploiting the utilization of solar energy. Polymer microsphres have also been used as templates for chemical synthesis and such chemical machining has been used to achieve visible wavelength photonic bandgap materials (Professor Younan Xie's pioneering work on photonic bandgap materials was featured on the cover of Advanced Materials (Adv. Mater., vol. 11, pages 2462-2466, 1999)). Dramatic advances have been made in the fabricating of phase-separating block copolymers. For the first time, such materials have been engineered to demonstrate a variety of electronic and optical functions much as described above for dendrimers. Significant advances have been made in the area of inorganic/organic nanocomposites and new materials have been used to fabricate high-density optical memories (including holographic and two-photon memories), organic lasers, and sensor protection materials. Substantial progress has been made in understanding intermolecular interactions that govern the assembly and organization of molecules into supramolecular structures. Progress has been made in developing external field processing methods for the realization of nanoscale architectures that cannot be achieved by molecular self-assembly.

The research of this center has received substantial acclaim in the scientific community. All but one of the investigators of this center have received major American Chemical Society awards since the establishment of the Center. Frechet has recently been elected to both the National Academy of Sciences USA and the National Academy of Engineering USA bringing the number of Academy members to three.

Final Research report of results obtained under AFOSR-MURI, Professor Larry R. Dalton

Nanoscale dendrimer and block copolymer materials have been synthesized in an effort to obtain electro-optic materials with dramatically improved properties [4,5,16,32,35,35,38-41,47,51,55,59,66,70]. In the case of dendrimers, this strategy of exploiting nanoscale

architectural engineering has worked very well with state-of-the-art electro-optic activities realized [66]. Indeed, electro-optic activity that is achieved with a given chromophore has been increased by a factor of two relative to that same chromophore incorporated into a polymer lattice. Moreover, the thermal and photochemical stability of electro-optic activity has been increased significantly. Also, dendrimers exhibit better solubility in traditional spin casting solvents and the control of molecular weight that is available with the dendritic synthesis approach permits better control of the viscosity of spin casting solutions. Chromophore-containing dendrimers are more easily incorporated into photonic bandgap lattices permitting the ready fabrication of devices appropriate for active wavelength division multiplexing (WDM) applications. The exploitation of dendritic electro-optic materials appears to be an important paradigm shift permitting the next level of performance to be achieved for this important class of materials. Interesting results have also been obtained for phase-separating block copolymer materials [4,5,24,32,35,38-41]; however, the inability to anneal microdomain structures currently limits the utility of such materials.

Significant progress has also been achieved in the synthesis, modification, processing, and device application of single wall carbon nanotube materials [69,unpublished—manuscript in preparation for submission to Science]. Actuators have been fabricated from these materials and optical switching has been demonstrated [unpublished results—present at SPIE]. Nanoscale fullerenes have also been investigated including for potential applications for sensor protection and optical switching [1,15,19,57]. Feasibility for all-optical signal processing at the telecommunications wavelength of 1.55 microns has been demonstrated [unpublished results—presented at SPIE]. The two-photon absorption coefficients of other materials, provide by AFRL-Wright Patterson, have also been characterized [8].

Nanostructured solar cell coatings and sensor materials have been developed and have been transitioned to AFRL-Kirtland and to Boeing [unpublished results—a number of manuscripts are currently in press]. Solar cell coatings are under continuing evaluation at AFRL-Kirtland but initial results are very promising. New sensor materials are already been commercially utilized by Boeing for the evaluation of the aerodynamics of airframes in wind tunnel testing. New organic light emitting diode (OLED) materials have also been prepared leading to state of the art efficiencies.

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73. L. Sun, J. Kim, C. Jang, D. An, X. Lu, Q. Zhou, J. M. Taboada, R. T. Chen, J. J. Maki, S. Tang, H. Zhang, W. H. Steier, C. Zhang, and L. R. Dalton, "Polymeric Waveguide Prism Based Electro-Optic Beam Deflector," Opt. Eng., 40, 1217-22 (2001).
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76. J. H. Kim, L. Sun, C.-H. Jang, D. An, J. M. Taboada, Q. Zhou, X. Lu, R. T. Chen, X. Han, S. Tang, H. Zhang, W. H. Steier, A. Ren, and L. R. Dalton, "Polymeric Waveguide Beam Deflector for Electro-Optic Switching," Proc SPIE, 4279, 37-44 (2001).

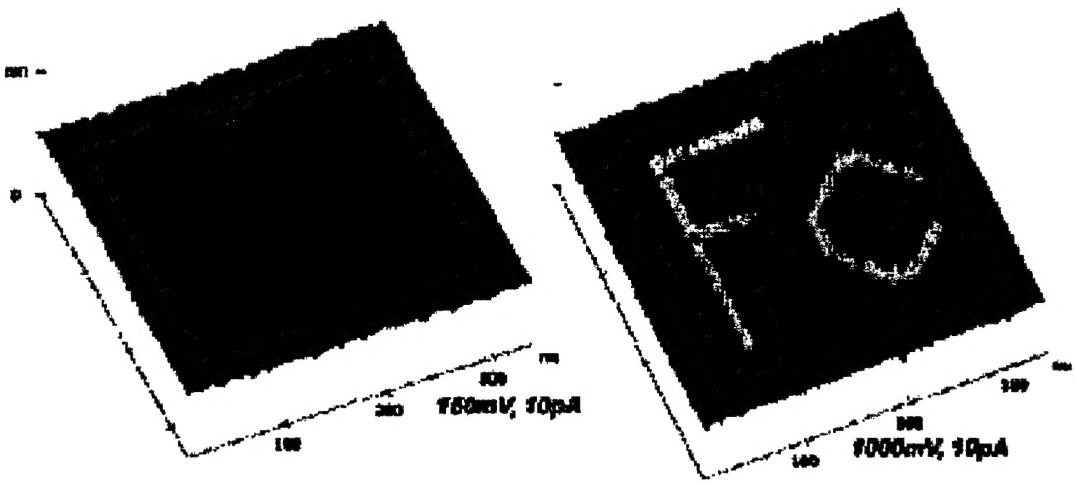
Final Research report of results obtained under AFOSR-MURI, Professor Christopher Gorman

Thirteen major publications were obtained under the MURI support. The work accomplished allowed us to accomplish the two major goals stated in the MURI proposal:

1. Illustrate how redox-active core dendrimers could be used in electronic encapsulation
2. Illustrate how probe-lithography on self-assembled monolayers could be used to prepare prototype molecular electronics devices.

More specific details of the work are given below:

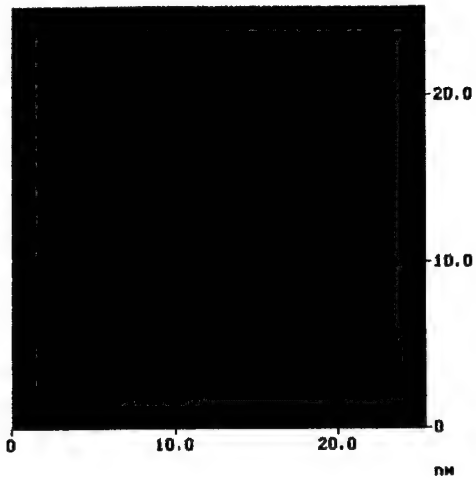
13. "Negative Differential Resistance in Patterned, Electroactive Self-Assembled Monolayers", Gorman, C. B.; Carroll, R. L.; Fuierer R., *Langmuir*, Accepted. – **Work will be featured on the 31 October 2001 cover of *Langmuir***



Abstract: The phenomenon of negative differential resistance (NDR) is potentially very useful in molecular electronics device schemes. In this work, we show for the first time that NDR can be observed in self-assembled monolayers composed of electroactive thiols on gold. Furthermore, these monolayers can be patterned using a scanning probe lithography technique described earlier to form a basis for potential molecular electronic device construction.

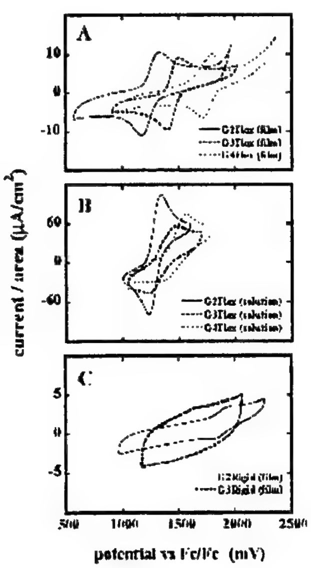
12. "The Influence of Head Group on the Structure of Self-Assembled Monolayers as Viewed by Scanning Tunneling Microscopy", Gorman, C. B.; He, Y.; Carroll, R. L., *Langmuir*, Accepted.

Abstract: Molecular resolution scanning tunneling microscopy images are shown of alkanethiol self-assembled monolayers (SAMs) containing alkene, cyano and carboxylic acid head groups. The alkene-terminated thiolate SAM displayed lattice structure indistinguishable from those of methyl-terminated thiol. The cyano-terminated thiolate SAM showed hexagonal, square and double row lattice structures, indicative of polymorphism and/or multiple chemical species on the surface. The carboxylic acid-terminated thiolate SAM showed a double row lattice structure very similar to that of the cyano-terminated thiolate SAM suggesting that perhaps the cyano groups had undergone hydrolysis to amide and/or carboxylic acid groups. This hypothesis was supported by the results of friction-force microscopy experiment on micro-contact printed patterns of these molecules.



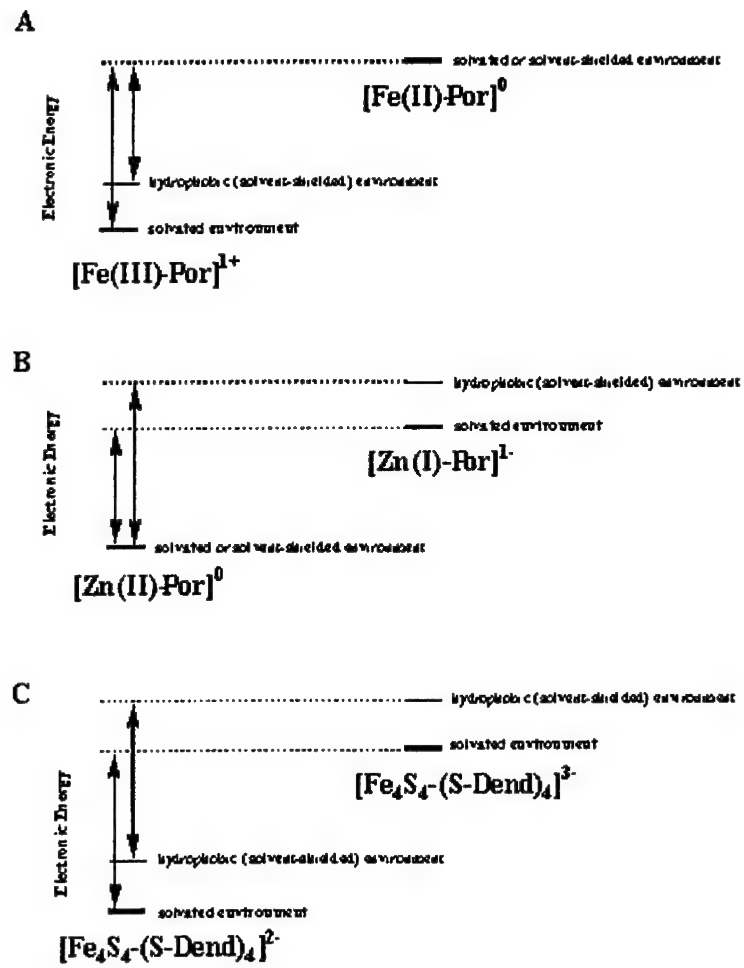
11. "Iron-Sulfur Core Dendrimers Display Dramatically Different Electrochemical Behaviors in Films Compared to Solution" Gorman, C. B.; Smith, J. C. *J. Am. Chem. Soc.*, **2000**; *122*(38), 9342-9343.

Abstract: Films of iron-sulfur cluster core dendrimers of varying generations displayed very different redox potentials (and thus thermodynamics of electron transfer) yet very similar electron transfer kinetics. This behavior is in sharp contrast to their electrochemical response in solution where the opposite trends were observed. This behavior is rationalized if the dendrimers provide an increasingly hydrophobic microenvironment with greater generation, thus influencing the redox potential yet the iron-sulfur redox units are sufficiently mobile within the dendrimer so that the effective unit-to-unit distance for electron transfer is not influenced much by generation.

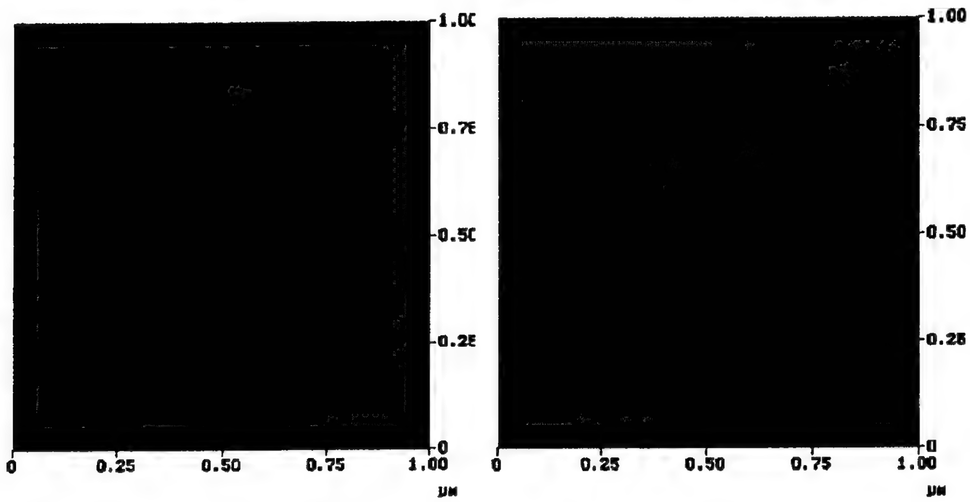


10. "Structure-Property Relationships in Dendritic Encapsulation", Gorman, C. B.; Smith, J. C., *Acc. Chem. Res.*, **2001**, *34(1)*, 60-71.

Abstract: Several molecular structure-property relationships are presented and compared to illustrate our current understanding of macromolecular encapsulation using dendrimers. Specifically, the effect that dendrimer architectures have on encapsulating photoactive and redox active units fixed at the molecular core is considered.



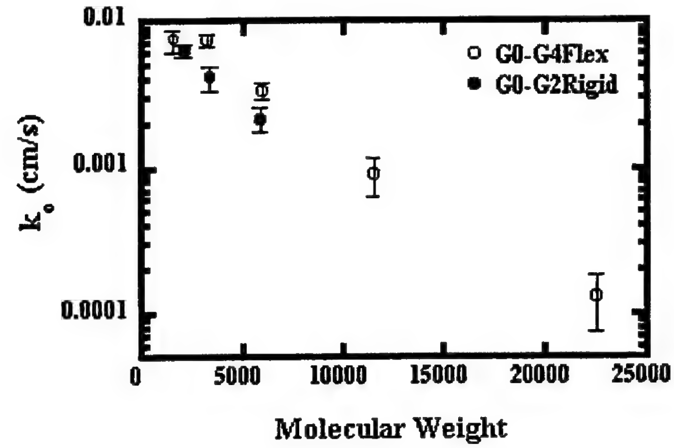
9. "Chemically Well-Defined Lithography using Self-Assembled Monolayers and Scanning Tunneling Microscopy in Non-Polar Organothiol Solutions", Gorman, C. B.; Carroll, R. L.; He, Y.; Tian, F.; Fuierer, R., *Langmuir*; **2000**; *16*(15); 6312-6316.



Abstract: A method of chemically well-defined, scanning tunneling microscope-based lithography is presented in which one thiolate in a self-assembled monolayer is removed and replaced with a second thiol. This method is distinguishable from other lithographic replacement processes on SAMs in that a nonpolar solution and an uncoated tip can be employed. Elevated relative humidity was important in the facility of this process, suggesting an electrochemical mechanism for replacement. The resolution of features written with this process is ca. 10-15 nm. In nonpolar solution, the apparent height differences between decanethiolate and dodecanethiolate self-assembled monolayers is reversed compared to images obtained in air. By exchanging the thiol solution after the first replacement, writing with two different thiols was demonstrated.

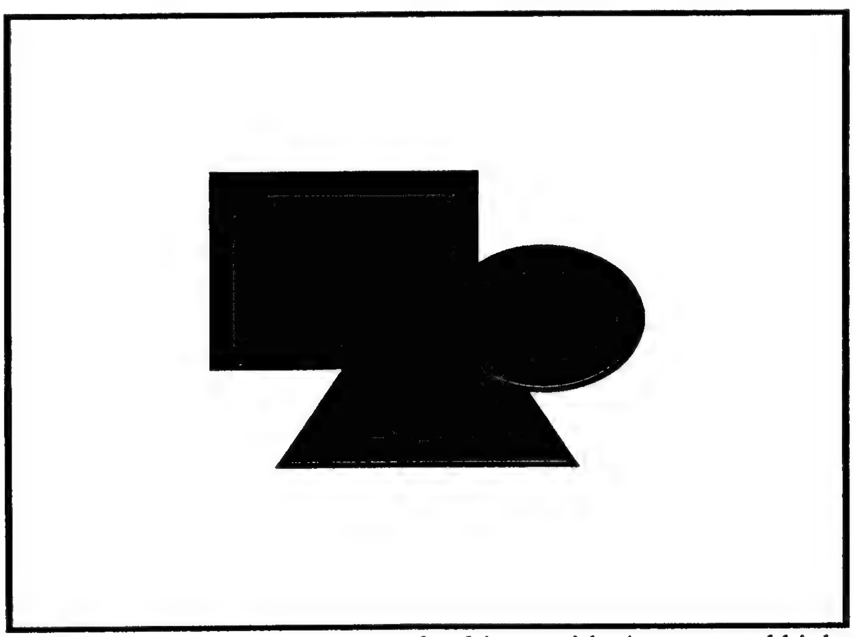
8. "Molecular Structure-Property Relationships for Electron Transfer Rate Attenuation in Redox-Active Core Dendrimers", Gorman, C. B.; Smith, J. C.; Hager, M. W.; Parkhurst, B. L.; Sierzputowska-Gracz, H.; Haney, C. A., *J. Am. Chem. Soc.*, **1999**, *121(43)*, 9958-9966.

Abstract: Two series of redox-active, iron-sulfur core dendrimers of the general structure $(nBu_4N)_2[Fe_4S_4(S\text{-}Dend)_4]$ (Dend = dendrons of generations 1 through 4) were prepared. Heterogeneous electron transfer rate constants indicated that the rigid series of dendrimers were more effective at attenuating the rate of electron transfer than were the flexible series of dendrimers. These results were rationalized using computationally-derived models which indicated an offset and mobile iron-sulfur core in the flexible series of molecules and a more central and relatively immobile iron-sulfur core in the rigid series of molecules. Further consideration of these data indicated that, while the dendrimers containing rigid ligands had better encapsulated redox cores for a given molecular weight, these molecules had higher electron transfer rates for a given molecular radius.

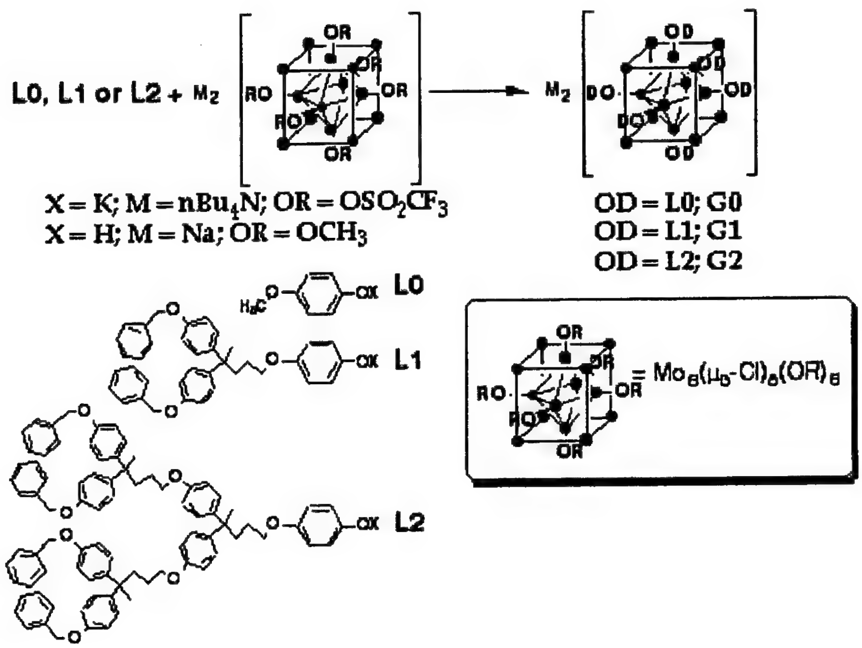


7. "Hybrid Organic-Inorganic, Hexa-arm Dendrimers Based on an Mo_6Cl_8 Core" Gorman, C. B.; Su, W. Y.; Jiang, H.; Watson, C. M.; Boyle, P., *Chem. Commun.*, **1999**, 877-878.

Abstract: Dendrons with focal phenoxide groups were shown to substitute for triflate or methoxide ligands around an Mo_6Cl_8 core to form molecules of the form $Mo_6(mu_3\text{-}Cl)_8(OR)_6$ where R = dendrons with zero through two hyperbranches, respectively. These molecules

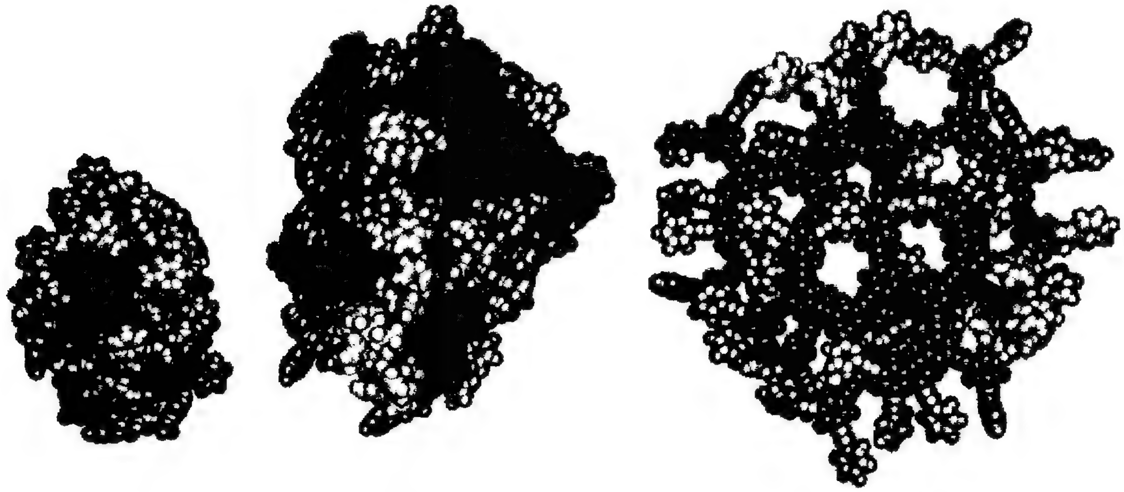


represent a new type of metal cluster core dendrimer with six arms and high symmetry.



6. "Effect of Repeat Unit Flexibility on Dendrimer Conformation as Studied by Atomistic Molecular Dynamics Simulations" Gorman, C. B.; Smith J. C., *Polymer*, **2000**, *41*, 675-683.

Abstract: The effect of repeat unit structure on the shape and internal organization of various dendrimers was probed using atomistic molecular dynamics simulations. In this technique, care was taken to ensure complete structural equilibration by implementing a high temperature dynamics/simulated annealing protocol prior to evaluation of the molecular structure and dynamics. Both flexible and stiff repeat units that have been employed previously in the synthesis of dendrimers were considered. Flexible-unit dendrimers were found to be globular but not completely spherical. In contrast, stiff-unit dendrimers had a more eccentric, disk-like shape. For all dendrimers, the different generations within each molecule were found to be radially distributed throughout its interior. This appearance could be attributed to back-folding of some of the repeat units in the flexible case and to a branching angle effect in the stiff case. This distribution, however, did not preclude a molecular surface composed of a substantial portion of the topologically terminal groups.



5. "Metallodendrimers: Structural Diversity and Functional Behavior" Gorman, C. B. *Adv. Mater.*, **1998**, *10,* 295-309. (Refereed, Invited Review).

Abstract: Metallodendrimers are an increasingly represented class of molecules in the area of dendrimer chemistry. Metal coordination has facilitated the synthesis of a number of dendritic, supramolecular structures. Moreover, the use of metals in dendrimer structures has resulted in molecules with potentially useful physical properties. In the most interesting cases, these properties are not found in the metal-bearing sub-unit of the dendrimer nor in an analogous non-metallated dendrimer. In this review, a number of metallodendrimers are presented with two general goals. First, as this class of molecules has substantial structural diversity, an attempt has been made to illustrate the various structure types. Metals have been incorporated in all of the topologically different parts of dendrimers. Examples will be shown in which metals are employed in the repeat or branching unit, at the molecular core, and at the peripheral units of the dendrimer. Second, metallodendrimers have begun to find applications, and several of these are highlighted here. In a few cases, a functional demonstration has been performed. In a number of other cases, work has illustrated a potentially useful physical property in a metallodendrimer, and some suggestion can be made of a functional behavior. As there are a number of examples in this latter class, it seems fair to say that, from a materials science perspective, the area of metallodendrimers is young but emerging.

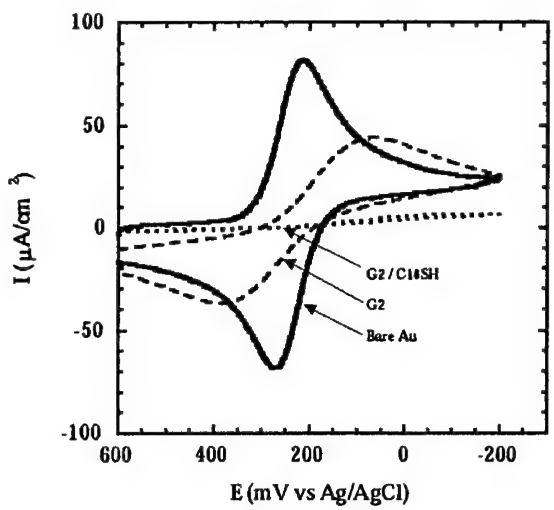
4. "Encapsulated Electroactive Molecules" Gorman, C. B. *Adv. Mater.*, **1997**, *9*, 1117-1119.

One application for dendrimers is the much-discussed molecular switch in which an electroactive moiety can be held alternatively in one of two binary states (corresponding to "on" and "off"). Any redox-active molecule is bistable in this regard and thus a candidate for a molecular switch. However, without encapsulation of some kind, facile electron transfer between closely spaced molecules or between molecules and a source for carrier injection can occur. This will result in the loss of stored information, particularly if the molecules are arranged in a closely spaced array such as would be desirable in an information storage (i.e. memory) demonstration. Thus, in this application, attenuation, or better, elimination of these electron transfer processes is necessary. Dendritic encapsulation is a potential molecule-based solution to this problem. The specific

question emerges, then, as to whether molecular structure-property relationships can be established that relate the structure and degree of branching in the dendrimer to the effectiveness or degree of electrical insulation (e.g. the degree of attenuation of the rate of electron transfer spoken in molecular terms).

3. "Semi-Permeable, Chemisorbed Adlayers of Focally-Substituted Organothiol Dendrons on Gold", Gorman, C. B.; Miller, R. L.; Chen, K.-Y.; Bishop, A. R.; Haasch, R. T.; Nuzzo, R. G., *Langmuir,* **1998**, *14*, 3312-3319.

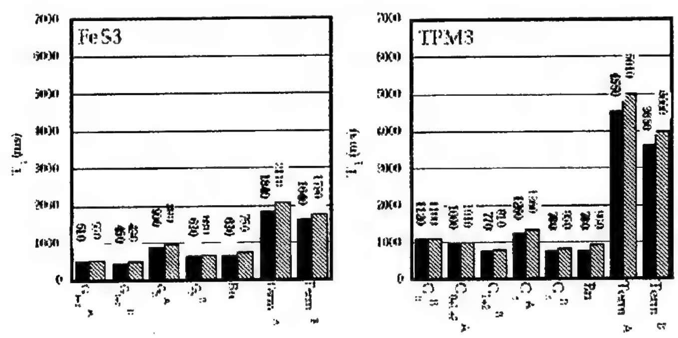
Abstract: A series of focally substituted organothiol dendrons of the first through third generation were used to construct adlayers on a gold surface. The presence and structural features of these adlayers were confirmed by X-ray photoelectron spectroscopy, infrared spectroscopy and ellipsometry. The relative coverage and/or permeability of these adlayers was studied using capacitance and electrochemical blocking experiments. It was found that, as the number of hyperbranches in the dendron increased from one to three, the dendron adlayers became initially less and then more permeable. This result indicated a tradeoff between size and packing efficiency when using these molecules to cover a surface. These data also suggest that the dendrons have formed homogenous but permeable adlayers on the gold surface rather than adlayers consisting of islands of material. These adlayers showed large differences in their ability to trap and hold a small molecule, *trans*-cyclohexanediol, within them.



2. "Use of a Paramagnetic Core to Affect Longitudinal Nuclear Relaxation in Dendrimers — A Tool for Probing Dendrimer Conformation" Gorman, C. B.; Hager, M. W.; Parkhurst, B. L.; Smith, J. C. *Macromolecules,* **1998**, *31*, 815-822.

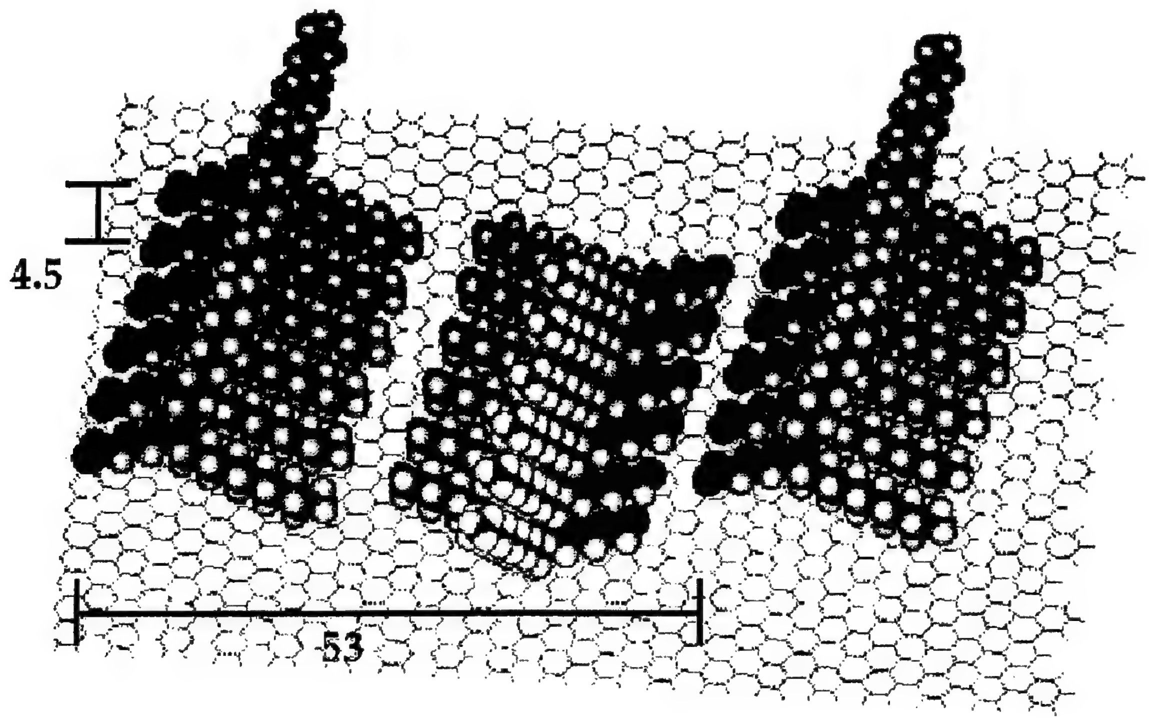
Abstract: The longitudinal relaxation time constants (T_1) of the protons in a series of dendrimers that alternatively had paramagnetic ($[Fe_4S_4(SR)_4]^{2-}$ R = dendron) and diamagnetic (tetraphenylmethane) cores were compared. The T_1 values of the phenyl and benzyl protons in

the paramagnetic core dendrimers were attenuated compared to analogous protons in the diamagnetic core dendrimers. This observation indicated that protons in each set of topologically different repeat units (generation) of the dendrimer approach the core of the molecule closely in space. This conclusion is consistent with the computed radial density distributions of the different generations calculated from molecular dynamics simulations. In addition, by comparing T_1 values of protons at two slightly different temperatures, the terminal groups in both sets of dendrimers were concluded to be, on average, more mobile than the other generations within the dendrimers. This conclusion is consistent with the computed mean square displacement correlation functions for the different generations also calculated from molecular dynamics simulations.



1. "Ordered Adlayers of a Non-Planar Molecule on a Surface: Misfit Monolayers and Intercalated Bilayers as the Result of a Dialkyl Amino Group", Gorman, C. B.; Miller, R. L., Touzov, I., *Langmuir*, **1998**, *14*, 3052-3061.

Abstract: Monolayer and bilayer structures of a nonplanar molecule, 5-(N,N-didecylamino)-2,4-pentadienal physisorbed onto highly oriented pyrolytic graphite have been characterized using several scanning probe techniques including scanning tunneling microscopy, and both contact and non-contact atomic force microscopy. These structures indicate several important components of this molecule in determining and enforcing an ordered packing motif that may be generalized to other supramolecular design schemes. In the monolayer structure, the geometry of the amino group enforces a motif in which part of the molecule lies upon the graphite surface and one of the alkyl chains extends away from the surface. This extended chain is a structure director for the formation of bilayer structures. The apparent thickness and stability of the bilayer structures are shown to be dependent on the presence of water or other admixtures, suggesting intercalation of small, polar molecules into this bilayer.



Final Report for the AFOSR-MURI Program

(Younan Xia, Department of Chemistry, University of Washington)

Technical Report:

Under the financial support of this MURI program, my group has been able to make a range of innovative contributions to the general area of nanostructured materials:

- We have demonstrated a method based on self-assembly for the large-scale fabrication of 3D photonic bandgap crystals. In this method, monodispersed spherical colloids (50 nm-10 um in diameter) were organized into 3D lattices, which were further used as templates to generate highly ordered porous materials with well-controlled pore sizes and structures. Due to the long-ranged, 3D order associated with these periodic structures, they exhibited photonic bandgaps in the optical regime whose positions could be controlled by changing the size of spherical colloids.
- We have developed several vectorial models for calculating the photonic bandgap structure of a self-assembled 3D system, and for describing the quantum electrodynamic (QED) processes that involve interactions between photons and 3D photonic crystals (such as the Lamb shift and spontaneous emission of chromophores imbedded in 3D photonic crystals). Previous models used in this area were all essentially scalar in nature that had neglected the vectorial nature of photons. We have also tried to combine the experimental studies and computational simulation, in an effort to elucidate the dependence of photonic bandgap properties on a set of parameters such as the shape and/or symmetry of the building blocks; the structural type of the periodic lattices; the contrast in refractive index between the high and low dielectric regions; and the lattice constant. The ultimate goal

is to accomplish a deep understanding on the structure-property relationship that can be used to guide the future design and synthesis of photonic crystals with pre-specified properties.

• My group has also demonstrated a few new approaches to the fabrication of nanostructures and synthesis of nanomaterials. The major goal of this work is to build a technology base for the large-scale production of nanostructures with well-controlled dimensions, well-defined shapes, and desired properties. For instance, my group has demonstrated a simple method based on soft lithography for high-volume production of nanostructures (e.g., wires, rods, and rings) of single crystalline silicon. My group has also demonstrated a solution-phase method based on controlled nucleation/growth for large-scale synthesis of well-defined nanowires of selenium, whose lateral dimensions could be varied in the range of 10-30 nm. At present, we are exploring the chemical and physical properties of these nanostructures, as well as their utilization in device fabrication.

This project has partially supported a number of postdoctors and graduate students over the past three years: post-doctors (Drs. S. H. Park, I. T. Kim, Z. Y. Zhong, M. Dreja, and Z. Y. Li); graduate students (B. Gates, Y. Yin, Y. Lu, and B. Mayers). We have published more than 25 scientific papers in refereed journals (including two invited review articles). There were also 3-4 undergraduate students involved in this project.

Awards and Honors:

Fellow in Science and Engineering, the David and Lucile Packard Foundation, 2000-2005
Sloan Research Fellow, the Alfred P. Sloan Foundation, 2000-2002
Faculty Early Career Development Award, the National Science Foundation, 2000-2004
Victor K. LaMer Award, the American Chemical Society, 1999
New Faculty Award, the Camille and Henry Dreyfus Foundation, 1997-2002

Awards received by graduate students working on this project: Byron Gates won two silver awards from the Materials Research Society (1999 and 2000); Yadong won one silver award from the Materials Research Society (2000)

List of Publications:

26 "Full Vectorial Model for Quantum Optics in Three-Dimensional Photonic Crystals", Li, Z.-Y. and Xia, Y., *Physical Review A* **2001**, *63*, 043817-1-11.

25 "Photonic Crystals", A special issue in *Advanced Materials* **2001**, *13*, 369.

24 "Fabrication of Three-Dimensional Photonic Crystals with Nonspherical Colloids as the Building Blocks", Lu, Y.; Yin, Y. and Xia, Y., *Advanced Materials* **2001**, *13*, 409-413.

23 "Self-Assembly Approaches to Photonic Bandgap Crystals", Xia, Y.; Gates, B. and Li, Z.-Y., *Advanced Materials* **2001**, *13*, 415-420.

22 "Optical Photonic Band Gaps and the Lamb Shift", Li, Z.-Y. and Xia, Y., *Physical Review B (Rapid Communication),* **2001**, *63*, 121305R.

21 "A Self-Assembly Approach to the Fabrication of Patterned, Two-Dimensional Arrays of Microlenses of Organic Polymers", Lu, Y.; Yin, Y. and Xia, Y., *Advanced Materials* **2001**, *13*, 34-37.

20 "Monodispersed Colloidal Spheres: Old Materials with New Applications", Xia, Y.; Gates, B.; Yin, Y. and Lu, Y., *Advanced Materials* **2000**, *12*, 693-713.

19 "Unconventional Methods for Fabricating and Patterning Nanostructures", Xia, Y.; Rogers, J. A.; Paul, K. and Whitesides, G. M., *Chemical Review* **1999**, *99*, 1823-1848 .

18 "A Soft Lithographic Approach to the Fabrication of Highly Ordered 2D Arrays of Magnetic Nanoparticles on the Surfaces of Silicon Substrates", Zhong, Z.; Gates, B.; Xia, Y. and Qin, D., *Langmuir* **2000**, *16*, 10369-10375.

17 "Crystallization of Mesoscopic Colloids into 3D Opaline Lattices in the Packing Cells Fabricated by Replica Molding", Mayers, B. T.; Gates, B. and Xia, Y., *Advanced Materials* **2000**, *12*, 1629-1632.

16 "A Soft Lithographic Approach to the Fabrication of Nanostructures of Single Crystalline Silicon with Well-Defined Dimensions and Shapes", Yin, Y.; Gates, B. and Xia, Y., *Advanced Materials* **2000**, *12*, 1426-1429.

15 "Fabrication and Characterization of Chirped Three-Dimensional Photonic Crystals", Gates, B. and Xia, Y., *Advanced Materials* **2000**, *12*, 1329-1332.

14 "Tuning the Photonic Bandgap Properties of Crystalline Arrays of Polystyrene Beads by Annealing at Elevated Temperatures", Gates, B.; Park, S. H.; Xia, Y., *Advanced Materials* **2000**, *12*, 653-656.

13 "Development of a Positive Pressure Driven Micro-fabricated Liquid Chromatographic Analyzer through Rapid-Prototyping with Poly(dimethylsiloxane) Optimizing Chromatographic Efficiency with Sub-Nanoliter Injections", Vahey, P. G.; Park, S. H.; Marquardt, B. J.; Xia, Y.; Burgess, L. W.; Synovec, R. E., *Talanta* **2000**, *51*, 1205-1212.

12 "Preparation of Mesoscale Hollow Spheres of TiO_2 and SnO_2 by Templating against Crystalline Arrays of Polystyrene Particles", Zhong, Z.; Yin, Y.; Gates, B. and Xia, Y., *Advanced Materials* **2000**, *12*, 206-209.

11 "Multilayered Supramolecular Structures Self-Assembled from Polyelectrolytes and Cyclodextrin Host-Guest Complexes", Dreja, M.; Kim, I. T.; Yin, Y. and Xia, Y., *Journal of Materials Chemistry* **2000**, *10*, 603-606.

10 "Fabrication of Ordered 2-D Arrays of Micro- and Nanoparticles Using Patterned Self-Assembled Monolayers as Templates", Qin, D.; Xia, Y.; Xu, B.; Yang, H.; Zhu, C. and Whitesides, G. M., *Advanced Materials* **1999**, *11*, 1433-1437.

9 "Fabrication and Characterization of Porous Membranes with Highly Ordered Three-Dimensional Periodic Structures", Gates, B.; Yin, Y. and Xia, Y., *Chemistry of Materials* **1999**, *11*, 2827-2836.

8 "Formation of Patterned Microstructures of Ceramics from Precursor Polymers Using Micromolding in Capillaries", Beh, W. S.; Xia, Y. and Qin D., *Journal of Material Research* **1999**, *14*, 3995-4003.

7 "Assembly of Nanoparticles into Opaline Structures over Large Areas", Gates, B.; Qin, D. and Xia, Y., *Advanced Materials* **1999**, *11*, 466-469.

6 "Fabrication of Three-Dimensional Photonic Crystals for Use in the Spectral Region from Ultraviolet to Near Infrared", Xia, Y.; Gates, B. and Park, S. H., *IEEE Journal of Lightwave Technology* **1999**, *17*, 1956-1962.

5 "A Three-Dimensional Photonic Crystal Operating in the Visible Region", Park, S. H.; Gates, B. and Xia, Y., *Advanced Materials* **1999**, *11*, 462-466.

4 "Crystallization of Meso-Scale Particles over Large Areas and Its Application in Fabricating Tunable Optical Filters", Park, S. and Xia, Y., *Langmuir* **1999**, 15, 266-273.

3 "Fabrication of Three-Dimensional Macroporous Membranes with Assemblies of Polymer Beads as Templates", Park; S. H. and Xia, Y., *Chemistry of Materials* **1998**, *10*, 1745-1747.

2 "Macroporous Membranes with Highly Ordered and Three-Dimensionally Interconnected Spherical Pores", Park, S. and Xia, Y., *Advanced Materials* **1998**, *10*, 1045-1048.

1 "Crystallization of Meso-Scale Particles over Large Areas", Park; S. H.; Qin, D. and Xia, Y., *Advanced Materials* **1998**, *10*, 1028-1032.

Final Research report of results obtained under AFOSR-MURI, Professor Paras N. Prasad

Twelve major publications were obtained under the MURI support. The work accomplished allowed us to achieve three major goals:

1. Design, synthesis and processing of multibranched structures, nanoparticles and nanocomposites with multifunctionality
2. Study of linear and nonlinear optical processes at nanoscopic level
3. Applications of nanostructured materials for photonics.

More specific details of the work are given below:

1. "Nanoscopic Study of Second-Harmonic Generation in Organic Crystals with Collection-Mode Near-Field Scanning Optical Microscopy", Shen, Y.; Markowicz, P.; Winiarz, J.; Swiatkiewicz, J.; Prasad, P. N., *Opt. Lett.*, **2001**, *26*(10), 725-727.

Abstract: Collection-mode near-field scanning optical microscopy (NSOM) was used to map nanoscopic second-harmonic generation (SHG) in *N*-(4-nitrophenyl)-(*L*)-prolinol nanocrystals. A spatial resolution of 98 nm is achieved. Near-field polarization-dependent SHG measurement was performed, and a local effective SHG susceptibility of 224 ± 18 pm/V was obtained.

2. "Nanophotonics: Interactions, Materials, and Applications", Shen, Y.; Friend, C. S.; Jiang, Y.; Jakubczyk, D.; Swiatkiewicz, J.; Prasad, P. N., *J. Phys. Chem. B*, **2000**, *104*, 7577-7587.

Abstract: This feature article presented our comprehensive study in the new area of nanophotonics, which deals with optical processes at the nanoscale, much smaller than the wavelength of optical radiation. Nanoscale matter–radiation interactions, which include nanoscale confinement of radiation, nanoscale confinement of matter, and nanoscale photophysical or photochemical transformation, offer numerous opportunities for both fundamental research and technological applications. We presented selected examples of our studies in each of these areas. Nonlinear optical interactions involving nanoscale confinement of radiation were theoretically analyzed and experimentally probed using a near-field geometry. Nanoscale confined optical domains to control excitation dynamics and energy transfer and to produce photon localization were illustrated by examples of nanostructured rare-earth-doped glasses, multiphasic nanocomposites, and photonic band gap materials. One application of nanophotonics presented here is the utilization of spatially localized photochemistry using a near-field excitation for nanofabrication and nanoscale memory. The article concluded with a discussion of the future outlook for nanophotonics.

3. "Silica Nanobubbles Containing an Organic Dye in a Multilayered Organic/Inorganic Heterostructure with Enhanced Luminescence", Lal, M.; Levy, L.; Kim, K. S.; He, G. S.; Wang, X.; Min, Y. H.; Pakatchi, S.; Prasad, P. N., *Chem. Mater.*, **2000**, *12*, 2632-2639.

Abstract: We reported the preparation, luminescent properties, and bioimaging applications of a novel zincsulfide (core)-two-photon dye–silica (shell) multilayered heterostructure. The method utilized reverse micelles synthesis involving multistep reactions as a result of which composite nanoparticles having different sizes and morphology were obtained. The size of these composite nanoparticles is typically 15-30 nm. An increase in the luminescence intensity (70 times higher) and in fluorescence lifetime was observed for the dye encapsulated within the silica nanobubble. Photobleaching results indicate that the dye is truly encapsulated and the silicon shell provides a barrier to penetration of oxygen, thereby making the dye more photostable. The application of these particles as nanoprobes for bioimaging of cells using two-photon laser scanning microscopy was also demonstrated.

4. "Nanoscale Chemistry and Processing of Multifunctional Composites for Nanophotonics and Biophotonics", Friend, C. S.; Lal, M.; Biswas, A.; Maciel, G. S.; Levy, L.; He, G. S.; Kim, K.-S.; Prasad, P. N., *Mol. Cryst. and Liq. Cryst.*, **2000**, *353*, 257-270.

Abstract: Multifunctional nanostructured materials and composites are of considerable interest for photonics, optoelectronics and biophotonics. This paper focused on three topics. The first part of the paper focused on silica encapsulated multifunctional nanoparticles. These particles show enhanced optical properties as well as photo, chemical and thermal stability. In the second part of the paper, we investigated the Er^{3+} sol-gel multicomponent silica glass prepared with nanostructure control for 1.55 μm amplification. These glasses demonstrate the longest

reported lifetime in sol-gel glasses to date, which we attribute to the reduction of the hydroxyl content in the glass. The third part of the paper presented our work on photonic crystals and methods to prepare them defect free.

5. "Second-Harmonic and Sum-Frequency Imaging of Organic Nanocrystals with Photon Scanning Tunneling Microscope", Shen, Y.; Swiatkiewicz, J.; Winiarz, J.; Markowicz, P.; Prasad, P. N., *Appl. Phys. Lett.*, **2000**, *77*(19), 2946-2948.

Abstract: Second-harmonic generation and sum-frequency generation with photon scanning tunneling microscopy and shear-force detection were used to map the nonlinear optical response and the surface topograph of *N*-(4-nitrophenyl)-(*L*)-prolinol nanocrystals with a subdiffraction-limited resolution. A domain-size dependence of the spatial feature was obtained, which shows the local orientational distribution of the optical near field radiated by nonlinear nanocrystals and reveals the difference between nanoscopic and macroscopic second-order optical nonlinearities of molecular crystals.

6. "Nanophotonics: Nanoscale Optical Science and Technology", Prasad, P. N.; Shen, Y.; Biswas, A.; Winiarz, J., in *Frontiers of Nano-Optoelectronic Systems*, Pavesi, L.; Buzaneva (eds.), Kluwer Academic Publishers, **2000**, 1-10.

Abstract: Nanophotonics, defined as nanoscale optical science and technology, is a new frontier, which includes nanoscale confinement of radiation, nanoscale confinement of matter, and nanoscale photophysical or photochemical transformation. Selected examples of our research work in each of these areas were presented. Nonlinear optical interactions involving nanoscale confinement of radiation was both theoretically and experimentally studied using a near-field geometry. The effort in nanoscale confinement of optical domains is focused to control excitation dynamics and energy transfer as well as to produce photon localization using nanostructured rare-earth doped glasses and novel inorganic-organic photorefractive nanocomposites. Spatially localized photochemistry using a near-field two-photon excitation was used for nanofabrication and nanoscale memory.

7. "Novel Two-Photon Absorbing Dendritic Structures", Adronov, A.; Fréchet; He, G. S.; Kim, K.-S.; Chung, S.-J.; Swiatkiewicz, J.; Prasad, P. N., *Chem. Mater.*, **2000**, *12*, 2838-2841.

Abstract: We synthesized the first two-photon dendrimer. These dendrimers were highly soluble in common organic solvents and were fully characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS. A linear correlation between the number of peripheral chromophores and the two-photon absorption cross-section of the molecule was found, indicating that there are neither cooperative nor deleterious effects in the dendrimers due to the high local chromophore concentration.

8. "Photogeneration, Charge Transport, and Photoconductivity of a Novel PVK/CdS-Nanocrystal Polymer Composite", Winiarz, J. G.; Zhang, L.; Lal, M.; Friend, C. S.; Prasad, P. N., *Chem. Phys.*, **1999**, *245*, 417-428.

Abstract: We reported on the photoconductive characteristics of the first inorganic:organic hybrid composite in which PVK serves as a polymeric charge-transporting matrix and quantum dots composed of surface passivated cadmium sulfide serve as a charge-generating sensitizer. The PVK:CdS nanocomposites prepared are directly compared with a similar composite composed of PVK and C_{60}, an extensively studied system due to its promising characteristics. We demonstrate the possibility of tuning the band-gap of these sensitizing nanocrystals through careful discretion in the method of synthesis such that their spectral response can be adjusted to suit a particular wave-length of operation. In this way materials can be fabricated which posses photoconductive characteristics exceeding those observed in the PVK:C_{60} system. Photosensitivity was studied and the Onsager formalism developed for organic systems was employed in order to extract the parameters r_o and $_o$ from the photocharge generation efficiency data.

9. "Spontaneous Reduction of Eu^{3+} Ion in Al Co-Doped Sol-Gel Silica Matrix During Densification", Biswas, A.; Friend, C. S.; Prasad, P. N., *Mat. Lett.*, **1999**, *39*, 227-231.

Abstract: Eu and Eu-Al co-doped silica glasses were prepared by impregnating the nanopores of a base catalyzed tetraethylorthosilicate (TEOS) gel with the nitrate salt of Eu and Al and subsequent densification around 1125 and

1150 C. Absorption, emission and excitation spectra of these glasses indicate that Eu^{3+} ions are spontaneously reduced to Eu^{2+} in the presence of Al^{3+} during sintering of the glasses above 1000 C.

10. "Observation of the Photorefractive Effect in a Hybrid Organic-Inorganic Nanocomposite", Winiarz, J. G.; Zhang, L.; Lal, M.; Friend, C. S.; Prasad, P. N., *J. Am. Chem. Soc.*, **1999**, *121*, 5287-5295.

Abstract: We reported the first observation of the photorefractive effect in an organic-inorganic polymer composite photosensitized with nanosized cadmium sulfide particles, the surface of which is passivated utilizing *p*-thiocresol. The semiconductor nanoparticles are dispersed in a poly(*N*-vinylcarbazole) (PVK) polymer matrix that also acts as the charge-transport species. The ability of these particles to behave as the photosensitizer in a PVK matrix was characterized through a dc photoconductivity experiment. In addition, for the photorefractive experiments, the second-order optically nonlinear chromophore 4-nitrophneyl-L-prolinol was also doped into the PVK matrix to elicit electro-optic response. Tricresyl phosphate was used to lower the glass-transition temperature of the material, allowing for room temperature in situ poling of the sample. In addition to the electric field dependence of the degenerate four-wave mixing diffraction efficiency, the photorefractive nature of the grating was confirmed via two-wave mixing asymmetric energy transfer. The paper also presented the methods employed in the syntheses of the capped CdS nanoparticles used in this study, which include the reverse micelle approach as well as competitive reaction chemistry. The resulting particles were characterized using UV-vis absorption and X-ray diffraction.

11. "Polymerization in a Reverse Micelle Nanoreactor: Preparation of Processable Poly(*p*-phenylenevinylene) with Controlled Conjugation Length", Lal, M.; Kumar, D.; Joshi, M. P.; Prasad, P. N., *Chem. Mater.*, **1998**, *10*, 1065-1068.

Abstract: We showed that a nanoscale polymerization reaction within the confinement of a reverse micellar cavity yields products with controlled conjugation lengths and, thus, controlled band gaps for applications to electronics and photonics. In addition, control of the physical size (length) of the polymer provided the prospects of monodispersity, improved processability, and preparation of nanocomposites. This novel approach was successfully applied to produce controlled chain length poly (*p*-phenylenevinylene) (PPV), a polymer that has drawn considerable attention in recent years for its electroluminescence, nonlinear optical, and lasing properties. Their linear optical properties and two-photon excited up-converted emission were characterized.

12. "Solid-State Cavity Lasing from Poly(*p*-phenylenevinylene)-silica Nanocomposite Bulk", Kumar, D. N.; Bhawalkar, J. D.; Prasad, P. N., *Appl. Opt.*, **1998**, *37*(3), 510-513.

Abstract: We fabricated inorganic-organic nanocomposite bulk samples consisting of poly(*p*-phenylenevinylene) (PPV) and silica by *in situ* polymerization of a PPV salt monomer within a porous glass using a base-catalyzed polymerization reaction and subsequent heat treatment. The samples processed at temperatures above 200 C showed a sharp reduction in fluorescence. Solid-state cavity lasing was achieved from the samples processed at 150 C with optical efficiency as high as 11.4%. We observed characteristic narrowing of the linewidth and the temporal profile.

MURI on Materials and Processing at the Nanometer Scale

Final Report (1995-2000)

G. K. Surya Prakash and George A. Olah

Technical Report:

Polymer nanospheres based on polystyrene and poymethylmethacrylates have attracted considerable attention in the field of immunology, combinatorial chemistry, protein supports, drug delivery, etc.[1] New uses in materials area such as magnets, polymer conductors, photonic band gap crystals, etc. are also being explored.[2] Although polymer nanospheres in the range 10 nm to 2 μM have been synthesized and studied, convenient methods for their surface functionalization and size control were still lacking. The method of choice for the preparation of polymer nanospheres is by emulsifier free emulsion polymerization of suitable monomers under aqueous conditions using radical initiators and cross-linking agents. With the MURI program, for the past five years, we have explored such techniques for the preparation of polymer nanospheres ranging from 160 nm to 1 μM using new monomers and conditions.

Initially, we fabricated monodispersed polystyrene nanospheres at the submicron diameter level (160 nm to 800 nm). The nanobeads in the 160-280 nm diameter levels when dispersed as thin films exhibit interesting refractive properties with light (exhibiting blue, green, red and violet colors). The color can be correlated to the diameter of the nanobead. Increase in size in the range led to a bathochromic shift. We have also functionalized the surface of the bead by a variety of functional groups such as –OH, NH_2, Br, Cl, -COOH and –SH by straight-forward aromatic functionalization techniques.

One of the problems of functionalizing pre-fabricated polystyrene nanospheres is that the chemistry for surface functionalization does not work very efficiently and surface coverage density is minimal. However, use of prefunctionalized monomer to fabricate the functionalized nanosphere is not economical and also the emulsifier free emulsion polymerization reaction may not work efficiently with functionalized monomers. To solve this problem, we have used the cross-linked polystyrene as the prefabricated bead (of required dimension) and the material was grafted with low concentration of the functionalized monomer (core shell approach). This approach is not only economical but also leads to surface functionalized nanospheres with diverse functional groups. With the new grafting technique we have coated the surface of a prefabricated polystyrene nanobead with a *para*-substituted styrene resulting in functionalized nanospheres. The *para*-hydroxystyrene grafted beads were used to complex silver and ruthenium nanoparticles.[3] Such functionalized polymer monodispersed nanobeads of varying sizes can be potentially used to fabricate photonic band gap materials for chemical sensors, wavelength modulators for optical communications, for some demonstration of unique energy transfer as well as standing wave phenomenon.

In collaboration with Professor Mark. E. Thompson, several different methods were also developed for the uniform coating of polystyrene beads with Pd, Pt and Au nanoparticles. These metal-derivatized spheres were also prepared with electroactive viologen groups. The metal immobilized spheres are further linked to 4-mercaptobutylphosphonic acid and subequently several multi-layers of ZrPV(Cl) (zirconium and N,N'-dialkyl-4,4"-bipyridinium chloride) were deposited by alternating Zr^{4+} and PV(Cl). Such multilayer bead system can be used as micro/nano reactors for the production of hydrogen peroxide from hydrogen and oxygen.[4]

Polymerization of both 2-vinyl and 4-vinylpyridines have resulted in nanospheres in the range of 500 nm. Pyridine nitrogens on the bead surface are excellent Lewis base donor sites and has been used to fabricate palladium coated nanospheres.[5] Such palladium coated nano-beads have also been used as catalysts for Suzuki and related oxidative coupling reactions.[4] The Pd coated beads exhibit significant thermal stability.

We have also developed $-CF_2SO_3H$ group attached polystyrene nanospheres resulting in superacidic nanospheres.[6] Such nanospheres have potential use as alkylation and isomerization catalysts.

The above described methodologies have led to mondispersed organic nanospheres whose surface properties can be suitably modified (hydrophobic, hydrophilic, cationically or anionically charged, metal coated, etc.). Such diverse beads can be utilized to complex specific proteins of varying nature. Our preliminary studies have shown that such protein bound nanobead can be directly used in a MALDITOF spectrometer and the mass spectrum of the attached protein can be obtained. A new collaborative venture with this new aspect has been established with Professor S. Rasheed at the USC School of Medicine.

An unexpected reaction of methyl benzoates with chlorotrimethylsilanes in the presence of magnesium led to the preparation of (3-oxo-3-phenyl)propylvinylsilanes. Such monomers can be used to make interesting polymeric architectures.[7]

A new methodology for the preparation of trifluoromethyl ketones from esters was also developed. The trifluoroacetyl group is a highly electron withdrawing moiety imparting novel electronic and optical properties to chromophores.[8]

Some new Fridel-Crafts functionalization of a smallest organic nanosphere, C_{60}, was also developed.[9]

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3. Poly *p*-Hydroxystyrene Grafted Polystyrene Nanospheres: Excellent hosts for Silver and Ruthenium Nanoparticles, M. Greci, S. Pathak, K. Mercado, G. K. S. Prakash, G. A. Olah and M. E. Thompson, *J. Nanoscience and Nanotechnology.* **2001**, 1, 3).

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5. Synthesis and Applications of Palladium Coated Polyvinylpyridine Nanospheres, Pathak, S., Greci, M., Kwong, R.C., Mercado, K., Prakash, G. K. S., Olah, G. A and Thompson, M. E. *Chem. Mat.* **2000**, *12*, 1985.

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9. Direct Preparation of Trifluoromethyl Ketones from Carboxylic Esters: Trifluoromethylation with Trifluoromethyltrimethylsilane, J. Wiedemann, T. Heiner, G. Mloston, G. K. S. Prakash and G. A. Olah, *Angew. Chem. Int. Ed.* **1998**, 37, 820.

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Publications acknowledging AFOSR Support:

1. Unexpected Reaction of Benzoates with Chlorovinylsilanes in the Presence of Magnesium: A Facile Synthesis of (3-oxo-3-phenyl)propylvinyl silanes and Further Transformations, E. C. Tongco, Q. Wang and G. K. S. Prakash, Synthesis, 1081 (1997).

2. Friedel-Crafts Reactions of Buckminsterfullerene, G. A. Olah, I. Bucsi, D. S. Haa, R. Aniszfeld, C. S. Lee and G. K. S. Prakash, Fullerene Science and Technolgy, 5, 389 (1997).

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Patents:

Nanoscale Solid Superacid Catalysts with Pendant Fluoroalkylsulfonic Acid or Fluoroalkylsulfonic Acid Groups, G. A. Olah and G. K. S. Prakash, US Patent, 5, 922,635, July 13, 1999.

G. K. Surya Prakash (Total Publications, 164, 1995-2000)

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4. N-Carboethoxypiperidine, A Convenient Preparation of Symmetrical Ketones from Organolithiums, G. K. S. Prakash, C. York, Q. Liao, K. Kotian and G. A. Olah, Heterocycles, 40, 79 (1995).

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G. K. Surya Prakash (Honors, Life time)

Research Excellence Award by the Loker Hydrocarbon Research Institute, University of Southern California, 1984.
Phi Kappa Phi Faculty Recognition Award for Research and Scholarship, University of Southern California, 1986.
AIST Guest Researcher, Osaka National Research Inst.(MITI), Japan, December 1993.
JPL/TAP Group Achievement Award for Direct Oxidation Methanol Fuel Cells, November 1994.
Visiting Researcher, National Institute for Resources and Environment (MITI), Tsukuba, Japan, January 16-26, 1996.
Guest Editor, Research on Chemical Intermediates, Issues 7, 8 and 9, 1996.
Advisory Editor, International Journal of Porphyrins and Pthalocyanines, 1997-2000.
First Holder of the George A. & Judith A. Olah Nobel Laureate Chair in Hydrocarbon Chemistry.
Visiting Professor, University of Pierre et Marie Curie, Paris 6, France, April -May 1998.
JPL/TAP Group Achievement Award for Low Crossover Membranes for Methanol Fuel Cells, December 1998.
USC Associates Award for Creativity in Research and Scholarship, University of Southern California, 2000.
Member of the Editorial Boards: Indian Journal of Chemistry, Section B, Journal of Organic Chemistry (American Chemical Society), and Journal of Nanoscience and Nanotechnology.

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Awards:

- American Chemical Society Award in Petroleum Chemistry, 1964
- Leo Hendrick Baekeland Award, 1967
- Morley Medal, 1970
- Fellow of the J. S. Guggenheim Foundation, 1972 and 1988
- Fellow of the Society for the Promotion of Science, Japan, 1974
- Member of the U.S. National Academy of Sciences, 1976
- Centenary Lectureship, British Chemical Society, 1977
- American Chemical Society Award for Creative Work in Synthetic Organic Chemistry, 1979.
- Alexander von Humbolt-Stiftung Award for Senior U.S. Scientists, 1979
- Foreign Member of the Italian National Academy dei Lincei, 1982
- Michelson-Morley Award of Case Western Reserve University, 1987
- Honorary Member Italian Chemical Society, 1988
- California Scientist of the Year Award, 1989
- American Chemical Society Roger Adams Award in Organic Chemistry, 1989
- Member of the European Academy of Arts, Sciences and Humanities, 1989
- Honorary Member Hungarian Academy of Sciences, 1990
- Richard C. Tolman Award, American Chemical Society, Southern California Section, 1992
- Chemical Pioneers Award, The American Institute of Chemists, Inc., 1993
- William Lloyd Evans Award, The Ohio State University, 1993
- Nobel Prize in Chemistry, 1994 (unshared).
- George Washington Award, American Hungarian Foundation, 1995
- Cotton Medal, American Chemical Society, Texas A&M, 1996
- Foreign Member, Russian Academy of Natural Sciences, 1996
- Member, American Academy of Achievement, 1996
- Kapitsa-Medal Russian Academy of Natural Sciences, 1996
- Inventor of the Year Award, New York Intellectual Property Lawyer Assoc., 1996
- The American Chemical Society renamed its annual Award in Petroleum as the "George A. Olah Award in Hydrocarbon or Petroleum Chemistry", 1996.
- Golden Plate Award, American Academy of Achievement, 1996.
- Foreign Member of the Royal Society of London, 1997.
- Foreign Member of the Royal Society of Canada, 1997.
- Government of Hungary Award for "The Promotion of the Renown of Hungary", 1997.
- Golden Medal of Charles University, Prague, Czech Republic, 1999.
- Hanus Medal, Czech Chemical Society, 1999.
- Honorary Fellow, Royal Society of Chemistry (London), 1999.
- Arthur C. Cope Award American Chemical Society 2001.

Honorary Degrees:

D.Sc. Honoris Causa, University of Durham, England, 1988; Technical University of Budapest, 1989; University of Munich, 1990; University of Crete, 1994; University of Jozsef Attila, Szeged, Hungary, 1995; University of Veszprém, Veszprém, Hungary, 1995; University of Southern California, Los Angeles, 1995; Case Western Reserve University, Cleveland, Ohio, 1995; University of Montpellier, Montpellier, France, 1996, State University of New York, 1998. University of Pecs, Hungary 2001.